

NO-A165 484

STUDIES OF NEGATIVE ION REACTIONS: SOLVATED IONS AND  
STRONG ACIDS(U) AIR FORCE GEOPHYSICS LAB HANSCOM AFB MA  
J F PAULSON ET AL. 07 MAR 86 AFGL-TR-86-0049

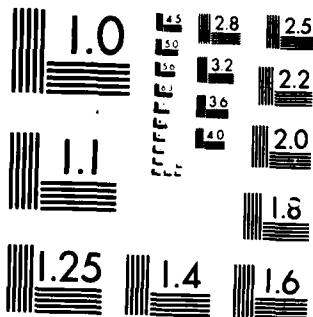
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AD-A165 484

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SYMPOSIUM ON ATOMIC  
AND SURFACE PHYSICS

86

# Contributions

EDITORS:

F. HOWORKA  
W. LINDINGER  
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Obertraun/Austria February 9 - 15

# STUDIES OF NEGATIVE ION REACTIONS : SOLVATED IONS AND STRONG ACIDS

John F. Paulson, Albert A. Viggiano<sup>1</sup>, Michael Henchman<sup>2</sup>, and Fred Dale,  
Air Force Geophysics Laboratory, Hanscom AFB, MA 01731

**Abstract :** The reactions of several negative ion species with up to three solvate molecules have been studied in a variable temperature selected ion flow tube. The reactions include association of some species of interest in the stratosphere and some proton transfer reactions of the strong and "super" acids.

## 1. Introduction

We have used a simple tightly enclosed electron impact ion source to generate both simple and solvated negative ions which can then be injected into a selected ion flow tube (SIFT). In the case of the solvated species, the core ions include  $\text{OH}^-$ ,  $\text{NO}_3^-$ , and  $\text{HSO}_4^-$ , and the solvates are  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$ . Although collisional dissociation of the injected solvated ions occurs to some extent in all but the most strongly bound clusters, useful number densities of several interesting solvated species can be obtained. We discuss here some reactions of both simple and solvated negative ions, including association of  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_m(\text{HNO}_3)_n$  with  $\text{HCl}$  and of  $\text{NO}_3^-$  with  $\text{HNO}_3$ , together with several reactions of strong Bronsted acids and their anions.

## 2. Experimental

The AFGL SIFT [3,4,5] is similar to that described by Adams and Smith [6]. The ion source is a stainless steel box measuring 2.5 by 1.5 by 1.5 cm. Electrons generated by an external filament of thoriated iridium or rhenium are accelerated by a potential of about 150V and enter the box through a hole 0.1 cm in diameter located at the center of a 2.5 by 1.5 cm face. A repeller electrode is located at the back of the source box. Primary negative ions are produced by dissociative attachment of both primary and secondary electrons. Subsequent ion-neutral collisions in the source generate higher order, e.g solvated, ions, which then exit the box through a hole 0.1 cm in diameter in the face opposite the repeller. Pressure in the

source may be as high as a few tenths of a torr. Sulfuric acid was admitted to the source by passing a carrier gas through glass wool saturated with the acid. The 'super' acids were simply heated to about 55°C where their vapor pressure is high enough to allow controlled flow. Nitric acid vapor was generated from a liquid mixture of 1 part HNO<sub>3</sub> and 2 parts H<sub>2</sub>SO<sub>4</sub> by volume.

### 3. Results and Discussion

#### Clustering in Stratospheric Ions

In situ ion composition measurements [7,8] have shown that the dominant negative ions in the stratosphere are NO<sub>3</sub><sup>-</sup>(HNO<sub>3</sub>)<sub>n</sub> and HSO<sub>4</sub><sup>-</sup>(H<sub>2</sub>SO<sub>4</sub>)<sub>m</sub>(HNO<sub>3</sub>)<sub>n</sub>. The species HCl is observed as a ligand in stratospheric ions and is a convenient one for laboratory study because of its high vapor pressure. We have measured rate coefficients [9] for the association of HCl with HSO<sub>4</sub><sup>-</sup>(H<sub>2</sub>SO<sub>4</sub>)<sub>m</sub>(HNO<sub>3</sub>)<sub>n</sub> for m=0 to 3 and n=0,1. At the lowest temperature (153K) and in either H<sub>2</sub> or He buffer, the rate coefficients for reactions of the unsolvated and singly solvated ions ranged from about 0.6(-26) to 2(-26) cm<sup>6</sup>s<sup>-1</sup>, while those for the doubly and triply solvated ions were below 0.04(-26) cm<sup>6</sup>s<sup>-1</sup>. The temperature coefficients of the clustering reactions, defined as n in the expression  $k_T = k_{300}(300/T)^n$ , were found to increase with increasing degree of solvation. A total of three ligands was found to bond strongly to HSO<sub>4</sub><sup>-</sup>.

In all instances of the clustering of HSO<sub>4</sub><sup>-</sup> core ions to HCl, the effective two-body rate coefficients varied linearly with pressure, indicating that the measurements were made in the low-pressure limit of three-body reactions. In contrast with these results, the effective two-body rate coefficient for the clustering of NO<sub>3</sub><sup>-</sup> with HNO<sub>3</sub> was found to be independent of pressure above 0.3 torr, and this reaction is therefore in the high pressure limit under these conditions. The fact that the rate coefficient, which is 2.5(-10) cm<sup>3</sup>s<sup>-1</sup> at 300K, is considerably lower than the collision limit has significant consequences for deriving stratospheric nitric acid concentrations from ion composition data. Using the present result, the nitric acid concentration at 40.8 km is about 65% higher than was estimated [10] assuming the collision limited rate coefficient.

## Ion Reactions of Some Strong Acids

In accord with precepts now over 60 years old, chemists are accustomed to think of acids in solution as being either good proton donors, as suggested by Bronsted and Lowry, or as good electron acceptors, as suggested by Lewis [11]. The application of the Lewis model to gas phase ion chemistry has been little explored, but the Bronsted/ Lowry model has been tested extensively. The gas phase acidity of a proton donor HX is defined as the enthalpy of the reaction in which the acid dissociates to form a proton and X<sup>-</sup>, i.e.,

$$\Delta H^{\circ}_{\text{acid}} = D(\text{H-X}) + \text{IP}(\text{H}) - \text{EA}(\text{X}) \quad (1)$$

In eq.(1), D(H-X) is the dissociation energy of HX, IP(H) is the ionization potential of H, and EA(X) is the electron affinity of X. Using this definition, stronger acids have lower values of  $\Delta H^{\circ}_{\text{acid}}$ . Gas phase acidities of a large number of molecules have recently been tabulated [12]. The strongest acid listed in this compilation is HI, for which  $\Delta H^{\circ}_{\text{acid}} = 314.6$  kcal/mol. The proton transfer reaction



is exothermic if

$$\text{EA}(\text{X}) + D(\text{H-Y}) \geq \text{EA}(\text{Y}) + D(\text{H-X}). \quad (2)$$

We have measured rate coefficients for several reactions involving strong acids in order to establish their relative acidities and to determine lower limits for the electron affinities, EA(X). Of particular interest are the species metaphosphoric acid (HPO<sub>3</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and the so-called "super" acids, trifluoromethylsulfonic acid (usually called triflic acid, CF<sub>3</sub>SO<sub>3</sub>H), and fluorosulfonic acid (FSO<sub>3</sub>H).

The results of these measurements are given in Table 1. These results may be summarized as follows. Triflic acid transfers a proton rapidly to each of the anions listed as reactants in reactions 1 to 5 and in addition undergoes an association reaction with FSO<sub>3</sub><sup>-</sup>. In its reaction with NO<sub>3</sub><sup>-</sup>·HNO<sub>3</sub>, both solvated and unsolvated product ions are observed.

Triflic acid is therefore a stronger acid than HI,  $\text{HPO}_3$ ,  $\text{FSO}_3\text{H}$ , and  $\text{H}_2\text{SO}_4$ . In reactions 6,7,and 9, fluorosulfonic acid transfers a proton to  $\text{I}^-$ ,  $\text{PO}_3^-$ , and  $\text{HSO}_4^-$ , and is therefore a stronger acid than HI,  $\text{HPO}_3$ , and  $\text{H}_2\text{SO}_4$ . Reactions 11 and 12 show that  $\text{H}_2\text{SO}_4$  is a stronger acid than HI and  $\text{HPO}_3$ . The failure of HI to transfer a proton to  $\text{PO}_3^-$  in reaction 16 suggests that  $\text{HPO}_3$  is a stronger acid than HI. The order of relative acidities is then  $\text{CF}_3\text{SO}_3\text{H} > \text{FSO}_3\text{H} > \text{H}_2\text{SO}_4 > \text{HPO}_3 > \text{HI}$ . The results in Table 1, together with literature values for the other required parameters, can be used in eq.(1) to conclude that the gas phase acidities of  $\text{CF}_3\text{SO}_3\text{H}$  and  $\text{FSO}_3\text{H}$  are similar and are both  $\leq 297$  kcal/mol.

The proton transfer reactions in Table 1 are a manifestation in the gas phase of acid-base chemistry familiar in liquid solutions. Proton transfer to an electron, which is completely equivalent to dissociative attachment, may also be considered as an acid-base reaction in which the electron is acting as a Bronsted base. It is of interest that dissociative attachment in the strong Bronsted acids has recently been discovered to be a rapid reaction [13].

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Table I. Rate Coefficients for Reactions of some Strong Acids.

Reaction			Rate Coefficient ( $10^{-9}\text{cm}^3\text{s}^{-1}$ )	
1. $\text{I}^-$	$+ \text{CF}_3\text{SO}_3\text{H} \rightarrow \text{CF}_3\text{SO}_3^- + \text{HI}$			2.4
2. $\text{PO}_3^-$	$+ \text{CF}_3\text{SO}_3\text{H} \rightarrow \text{CF}_3\text{SO}_3^- + \text{HPO}_3$			3.2
3. $\text{FSO}_3^-$	$+ \text{CF}_3\text{SO}_3\text{H} \rightarrow \text{CF}_3\text{SO}_3^- + \text{FSO}_3\text{H}$	75% 70%		2.5
	$\rightarrow \text{CF}_3\text{SO}_3^-(\text{FSO}_3\text{H})$	25% 30%		
		0.4 0.8 torr		
4. $\text{HSO}_4^-$	$+ \text{CF}_3\text{SO}_3\text{H} \rightarrow \text{CF}_3\text{SO}_3^- + \text{H}_2\text{SO}_4$			2.8
5. $\text{NO}_3^-(\text{HNO}_3)$	$+ \text{CF}_3\text{SO}_3\text{H} \rightarrow \text{CF}_3\text{SO}_3^- + 2\text{HNO}_3$	50%		2.6
	$\rightarrow \text{CF}_3\text{SO}_3^-(\text{HNO}_3) + \text{HNO}_3$	50%		
6. $\text{I}^-$	$+ \text{FSO}_3\text{H} \rightarrow \text{FSO}_3^- + \text{HI}$			2.0
7. $\text{PO}_3^-$	$+ \text{FSO}_3\text{H} \rightarrow \text{FSO}_3^- + \text{HPO}_3$			1.5
8. $\text{CF}_3\text{SO}_3^-$	$+ \text{FSO}_3\text{H} \rightarrow \text{CF}_3\text{SO}_3^-(\text{FSO}_3\text{H})$			1.2
9. $\text{HSO}_4^-$	$+ \text{FSO}_3\text{H} \rightarrow \text{FSO}_3^- + \text{H}_2\text{SO}_4$			1.3
10. $\text{NO}_3^-(\text{HNO}_3)$	$+ \text{FSO}_3\text{H} \rightarrow \text{FSO}_3^- + 2\text{HNO}_3$	15%		1.3
	$\rightarrow \text{FSO}_3^-(\text{HNO}_3) + \text{HNO}_3$	85%		
11. $\text{I}^-$	$+ \text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^- + \text{HI}$			1.9
12. $\text{PO}_3^-$	$+ \text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^- + \text{HPO}_3$			2.4
13. $\text{FSO}_3^-$	$+ \text{H}_2\text{SO}_4 \rightarrow \text{FSO}_3^-(\text{H}_2\text{SO}_4)$			2.4
14. $\text{CF}_3\text{SO}_3^-$	$+ \text{H}_2\text{SO}_4 \rightarrow \text{CF}_3\text{SO}_3^-(\text{H}_2\text{SO}_4)$			1.5
15. $\text{NO}_3^-(\text{HNO}_3)$	$+ \text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^- + 2\text{HNO}_3$	<15%		2.4
	$\rightarrow \text{HSO}_4^-(\text{HNO}_3) + \text{HNO}_3$	>85%		
16. $\text{PO}_3^-$	$+ \text{HI} \rightarrow \text{PO}_3^-(\text{HI})$			0.0068



## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY STATEMENT A		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE			Approved for public release Distribution Unlimited		
4. PERFORMING ORGANIZATION REPORT NUMBER(S)  AFGL-TR-86-0049			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Air Force Geophysics Laboratory		6b. OFFICE SYMBOL (If applicable)  LID	7a. NAME OF MONITORING ORGANIZATION		
6c. ADDRESS (City, State, and ZIP Code) Hanscom AFB Massachusetts 01731			7b. ADDRESS (City, State, and ZIP Code)		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2303	TASK NO. G1
			WORK UNIT ACCESSION NO. 10		
11. TITLE (Include Security Classification) Studies of Negative Ion Reactions: Solvated Ions and Strong Acids					
12. PERSONAL AUTHOR(S) John F. Paulson, Albert A. Viggiano, Michael Henchman, and Fred Dale					
13a. TYPE OF REPORT Reprint		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) 1986 March 7	
				15. PAGE COUNT 5	
16. SUPPLEMENTARY NOTATION Reprinted from SASP Symposium on Atomic and Surface Physics '86 Obertraun/Austria February 9-15					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
			Nitric acid      Triflic Acid      Ion clustering		
			Sulfuric acid      Fluorosulfanic acid		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)  The reactions of several negative ion species with up to three solvate molecules have been studied in a variable temperature selected ion flow tube. The reactions include association of some species of interest in the stratosphere and some proton transfer reactions of the strong and "super" acids.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>		
22a. NAME OF RESPONSIBLE INDIVIDUAL J.F. PAULSON			22b. TELEPHONE (Include Area Code) (617) 861-3124		22c. OFFICE SYMBOL LID

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